

**METHOD FOR PRINTING ETCH MASKS USING PHASE-CHANGE  
MATERIALS**

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**BACKGROUND**

5 In recent years, the increasingly widespread use of display device alternatives to the cathode ray tube (CRT) has driven the demand for large-area electronic arrays. In particular, amorphous silicon and laser recrystallized poly-silicon are used to drive liquid crystal displays commonly used in lap-top computers. However, fabricating such large-area arrays is expensive. A large part of the  
10 fabrication cost of the large-area arrays arises from the expensive photolithographic process used to pattern the array. In order to avoid such photolithographic processes, direct marking techniques have been considered an alternative to photolithography.

Examples of direct marking techniques used in place of photolithography include utilizing a xerographic process to deposit a toner that acts as  
15 an etch mask and using an ink-jet printhead to deposit a liquid mask. Both techniques have corresponding problems. Toner materials are hard to control and difficult to remove after deposition while controlling feature size of a printed liquid mask is difficult.

Small printed features have been obtained using ink-jet printheads.  
20 Special piezoelectric ink-jet printheads allow generation of low droplet volumes. However, even with the special printhead, the small size of features critical to the fabrication of large-area arrays has been difficult to achieve because of the surface tension between the droplet and the wetted surface. Typically, complete wetting is needed to form a good contact in order to prevent undercutting of the printed mask.  
25 However, as the surface is wetted, the liquid droplet tends to spread out making it difficult to control feature size. When used to pattern elements on a substrate, the droplet spreading results in undesirably large printed feature sizes. Decreasing the

wetting properties of the substrate surface results in unreliable patterning due to poor adhesion of the droplet to the substrate. The poor adhesion can cause defects such as discontinuities in lines being fabricated. Variation in wetting properties across a substrate also presents problems as the droplet size must be adjusted to accommodate  
5 different materials to be patterned.

Thus an improved method for masking a substrate to be etched is needed.

### SUMMARY OF THE INVENTION

10 The present invention relates generally to the field of device processing. In particular the invention relates to a method and apparatus for masking a surface by ejecting droplets of a phase-change masking material from a droplet source onto a surface to be modified or etched. In order to avoid extended wetting and still achieve improved adhesion between the masking material and the surface to be  
15 etched; the surface is maintained at a temperature such that the masking material remains in a liquid phase for only a brief period after contact with the surface.

In one embodiment of the invention, the temperature of the surface to be etched is maintained below the freezing point of the phase-change masking material such that after deposition, the masking material rapidly converts from a liquid  
20 to a solid. In a second embodiment, the temperature of the surface to be etched is maintained above the boiling point of a liquid that carries a suspended masking material such that the liquid carrier rapidly evaporates after contact with the surface to be etched. One particularly suitable embodiment of the invention utilizes a phase-change organic material that solidifies at room temperature making such phase-change  
25 organic materials suitable for room temperature operation of the described processes.

After deposition of the masking material, the surface is etched to remove material not masked by droplets of the phase-change masking material. After etching the surface masked by the phase-change masking material, the phase-change masking material is removed from the surface.

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### BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention may be more readily understood by referring to the detailed description and the accompanying drawings.

Fig. 1 shows a system that controls substrate temperature while  
10 depositing a phase-change-masking material onto the substrate in preparation for substrate etching.

Fig. 2 shows one embodiment of a droplet source used in the system of Fig. 1. to eject a phase-change material onto a substrate.

Fig. 3 is a side view of several droplets as a function of the amount of  
15 wetting that occurs.

Fig. 4 is a top level view of a line formed by ejecting droplets of phase change material.

Fig. 5 is a flow chart showing the operations involved in using a phase change masking material in a direct mask process.

Fig. 6 is a flow chart showing the operations when using a phase  
20 change masking material in a sacrificial layer patterning of a substrate.

Fig. 7 is a flow chart showing the operations when using a phase change masking material in a photolithographic process.

## DETAILED DESCRIPTION

In the following detailed description a method and system of masking a substrate will be described. The system will control the temperature of a surface to be etched such that when a droplet source deposits droplets of phase-change masking material onto the surface of the substrate to be etched, the droplets remain in a liquid state for only a very brief period of time. In one embodiment, this is achieved by maintaining the temperature of the substrate below the freezing point of the phase change masking material.

As used herein, the term "phase-change masking material" refers to compounds or elements that changes in phase from a liquid to a solid, or in some embodiments from a liquid to a gas. In one embodiment of the invention, the phase change material have low melting points (also called freezing point) below 150 °C with a narrow transition temperature range. The phase-change masking material may also be mixtures or dispersions without precise freezing temperatures. However, even without specific freezing temperatures, these materials still retain the characteristic of transitioning from a substantially liquid phase to a substantially solid phase in a narrow temperature range. In one particular embodiment of the invention, the phase change material is an organic material such as a wax that has a melting point between 60 degrees and 100 degrees centigrade. Even aqueous solutions may be used as a phase-change mask material when the substrate temperature is kept below the freezing point of the liquid. For example, water may be ejected onto a substrate that is maintained at a temperature below zero degrees centigrade.

The temperature of the substrate is maintained such that upon contact with the substrate, the liquid droplets of phase-change material is quenched and rapidly converts from a liquid state to a solid state. As will be further described, adjusting substrate temperature changes the quench rate. In one embodiment of the invention, the quench rate, and thus the substrate temperature is dynamically adjusted

depending on the feature size to be printed. When smaller features are needed, the substrate surface is cooled even further below the freezing point of the phase change material resulting in a high quench rate. The high quench rate causes the droplet to freeze almost instantaneously upon contact with the substrate surface resulting in a small feature size. A larger feature size may be achieved by raising the substrate temperature to only slightly below the phase change material freezing point. The raised temperature lowers the quench rate such that the droplet spreads before freezing.

The difficulty of maintaining the substrate below the freezing point of the masking material is one criterion to be considered in determining what phase change material should be used. In some applications, the surface of the substrate is maintained at least 10 degrees below the freezing point of the phase-change masking material to assure rapid conversion from a liquid to a solid state. However, maintenance of the substrate at such temperatures may be undesirable or inconvenient for some semiconductor processes. For example, cooling and maintaining a substrate at negative 10 degrees centigrade throughout the deposition and subsequent etching process may interfere with the etching process. In such situations, organic materials are particularly convenient, because the melting point of such materials allows the substrate to be maintained at room temperature (approximately 30 degrees centigrade) and still meet the criteria of rapid freezing of the masking material after deposition on the surface to be etched. In particular, the approximately 60 degree melting point of many waxes is almost 30 degrees above a substrate maintained at a room temperature of 30 degrees. Due to the practicality of using phase change organics, the remainder of the specification will discuss using such materials in the deposition process, although it is to be understood that other phase change materials may be used.

After deposition of the phase-change masking material on a surface of the substrate, the substrate or thin film is etched resulting in removal of material not

protected by the phase-change masking material. After etching of the substrate, the masking material is removed.

Figure 1 shows a system 100 including a heat source 104 that heats a reservoir 108 of phase-change masking material to a temperature that is sufficient to maintain the phase change masking material in a liquid state. In one embodiment of the invention, the temperature of the reservoir is maintained above 100 degree centigrade and in some embodiments, at temperatures above 140 degrees centigrade, a temperature sufficient to liquify most phase change organics.

As previously discussed, the phase-change masking material may be an organic media that melts at low temperatures. Other desirable characteristics of the phase-change masking material include that the masking material is non-reactive with inorganic materials used in typical semiconductor materials processing, and has a high selectivity to etchants. An alternate embodiment of the invention may also include a masking material suspended in a liquid. When liquid suspension is used, the substrate material is maintained above the boiling point of the liquid, and after deposition of the masking material, the liquid carrier evaporates upon contact with the substrate surface. When evaporation is used, the phase change process is directed from liquid to vapor, rather than from liquid to solid.

An additional characteristic of the phase-change masking material is that the resulting mask should be robust enough to withstand wet-chemical or dry etching processes. When a dry etching process is used, phase change masking materials with low-vapor pressures may be used. Wax is an example of a phase-change material with the previously described characteristics. Kemamide 180-based waxes from Xerox Corporation of Stamford Connecticut is one example of a suitable wax for use as a phase-change masking material.

A plurality of droplet sources such as droplet source 112 receives the liquid phase-change marking material from reservoir 108 and outputs droplets 116 for

deposition on a substrate 120. The substrate is typically a thin film of semiconductor material or a thin-film metal such as aluminum. The substrate is maintained at a temperature such that the droplet cools rapidly after deposition. In some embodiments of the invention, a wetting agent, typically a dielectric material such as silicon dioxide, SiO<sub>2</sub> or silicon nitride, Si<sub>3</sub>N<sub>4</sub> may be included on the surface to assure that sufficient wetting occurs to make a good contact between the mask and the substrate. Despite the enhanced wetting, the rate of cooling is sufficient such that the behavior of the droplet after contacting substrate 120 is controlled more by the cooling rate of the liquid than the wetting properties of the substrate surface to be etched.

The substrate temperature controls the rate of cooling. When increased coalescence between adjacent droplets is required, the substrate temperature can be increased to increase droplet spreading and thereby increase coalescence. When printing lines of Kemamide wax from an acoustic ink-jet printer, it has been found that increasing the substrate temperature from 30 degrees to 40 degrees centigrade improved the print quality of the mask. However, the temperature of the substrate is still kept low enough such that the droplet solidifies or rapidly "freezes" upon contacting substrate 120. Thus in the case of Kemamide wax, it was found that excellent results were achieved when the substrate was maintained at approximately 20 degrees centigrade below the freezing point of the wax.

In order to minimize the possibility of partial midair freezing of droplets in space 121 between droplet source 112 and substrate 120, an electric field 122 may be applied to accelerate the droplet from droplet source 112 to substrate 120. The electric field may be generated by applying a voltage, typically between one to three kilovolts between droplet source 112 and a platen 122 under substrate 120. The electric field minimizes droplet transit time through space 121 and allows substrate surface temperature to be the primary factor controlling the phase change operation. Moreover, the increased droplet velocity in space 121 improves the directionality of the droplet allowing for improved straight-line features.

After a droplet of marking material is deposited on substrate 120, the relative positions of the substrate and the droplet source are adjusted to reposition the droplet source over a second position to be masked. The repositioning operation may be achieved either by moving droplet source 112 or by moving substrate 120. In the  
5 illustrated embodiment, a control circuit 124 moves droplet source 112 in a predetermined pattern over substrate 120. A driver circuit 128 provides energy to droplet source 112 causing ejection of droplets when droplet source 112 is positioned over a region of substrate 120 to be masked. By coordinating the movement of droplet source 112 with the timing of droplet source outputs, a masking pattern can be  
10 "printed" on the substrate.

As each drop is printed, a feedback system may be used to assure droplets of proper size. An imaging system, such as camera 122, may be used to monitor droplet size. When smaller features are to be printed, or the droplet size otherwise reduced, a temperature control circuit 123 lowers the temperature of a  
15 surface of substrate 120. The lower temperature increases the quench rate resulting in rapid solidification of the phase change masking material upon contact with substrate 120. When larger droplets are needed, usually for merging droplets in larger features, temperature control circuit 123 raises the temperature of substrate 120. In one embodiment of the invention, temperature control circuit 123 includes a heating  
20 element thermally coupled to substrate 120 such that ambient heating of media around the substrate is minimized.

In one embodiment of the invention, the phase change material is a solid at temperatures below approximately 60 degrees centigrade. In such embodiments, it may be unnecessary to cool the substrate below room temperature  
25 because as previously described, a sufficiently small droplet cools rapidly when a 20 degree temperature differential is maintained between the freezing point of the phase change material and the substrate temperature. In such cases, the temperature control



circuit may merely be a sensor and a heater that raises the substrate slightly above room temperature when larger feature sizes are to be printed.

In order to control and align the movement of droplet source 112, printed alignment marks, such as mark 113, patterned from a previous mask layer may be used to coordinate the next overlying mask layer. An image processing system such as the previously described camera may be used to capture the orientation of the previous mask layer. A processing system then adjusts the position of the overlying mask layer by altering the mask image file before actual printing of the mask layer. In this way, the substrate remains fixed and mechanical movement of the substrate holder is unnecessary. Instead positioning adjustment are accomplished in software and translated to movements of droplet source 112.

Each droplet source may be implemented using a variety of technologies including traditional ink-jet technology. An alternative technology well suited for generating extremely small droplet sizes is the use of sound waves to cause ejection of droplets of masking material as done in acoustic ink printing systems. Figure 2 shows one embodiment of an acoustic droplet source 200 implemented using acoustic ink printing technology.

In Figure 2, a source of acoustic waves such as piezo electric driver 204 generates acoustic waves 208 in a pool 212 of phase change masking material. Acoustic lens 216 focuses the acoustic waves such that a droplet of phase change masking material is ejected from the surface of pool 212. The droplet is deposited on substrate 120 of Figure 1.

Figure 3 shows a side view of printed droplets 304, 308, 312. First droplet 304 illustrates the shape of the droplet when insufficient wetting occurs. The droplet is almost entirely round resulting in minimal contact area 306 between substrate 300 and first droplet 304. The minimal contact area produces poor adhesion between droplet 304 and substrate 300.

Second droplet 308 illustrates the effect of excessive wetting. When excessive wetting occurs, the droplet is almost planar with the surface of substrate 300. Although adhesion is excellent, the spreading results in large feature sizes. Third droplet 312 illustrates a droplet under proper wetting conditions. Third droplet 312 adheres tightly to the substrate 300 while still maintaining reasonable curvature associated with smaller droplet areas used to mask smaller features.

Figure 4 shows a top view 400 of a substrate 402 with three printed lines 404, 408, 412 of printed phase change organic masking material. The first line 404 is printed while the substrate is at a first lowest temperature of approximately 50 degrees centigrade, the second line 408 at a second middle temperature of approximately 60 degrees centigrade, and the third line 412 is printed while the substrate is at a high temperature of approximately 70 degrees centigrade. At the first temperature, droplets 416, 420 are at the smallest size. At the middle temperature in line 408, droplets 424, 428 spread to merge together and form a line. At the high substrate temperatures used in printing line 412, excessive spreading results in undesirably large droplets as exemplified by droplets 432, 436. Further raising the temperature of substrate 402 can result in the droplets combining to form continuous lines 440. Excessively high substrate temperatures can result in merging of lines to create pads 444.

Figure 5 is a flow diagram 500 showing the operations involved in patterning a surface using a direct mask process. In block 504, a thin film that acts as a substrate to be patterned is deposited over a support structure. The phase-change material, in this case a wax is then printed over the thin film. Blocks 508 to 524 define this printing process.

In block 508, the wax is heated to a temperature sufficient to liquify the phase-change material. The substrate is also heated to an optimal temperature as described in block 512. The optimal substrate temperature causes rapid "freezing" of

ejected droplets that contact the thin-film surface. The actual optimal temperature is typically determined by the desired feature size, smaller feature sizes will result in a lower substrate temperature to produce a higher quench rate.

In block 516, a droplet source outputs a droplet of the phase-change material. The droplet source output may be generated by using piezo-electric transducers to generate acoustic waves that cause ejection of a droplet. Alternate embodiments use combined methods of ink-jet printing technology to cause ejection of a droplet. Examples of ink-jet printing technology include piezoelectric and thermal ink-jet technologies. However, the process is not limited to these types of printheads, rather the phase-change material may be dispensed by any conventional droplet ejection technique. The droplet is directed towards and deposited upon the thin-film or the substrate surface.

In some embodiments, a feedback loop may be used to determine if the deposited droplet is properly spread over the substrate. In such embodiments, a detection system, such as a camera in an imaging system, determines the amount of droplet spreading that occurred after deposition as described in block 517. When in block 518, it is determined that the droplet size spreading is insufficient, resulting in a coverage area that is too small, the substrate temperature is increased in block 519. When in block 521, it is determined that the droplet size spreading is excessive, resulting in a coverage area that is too large, the substrate temperature is reduced in block 522.

In block 520, circuitry that controls movement of the droplet source determines if the masking pattern has been completely printed. When the pattern has not been completely printed, the droplet source is repositioned in block 524. The operations of repositioning and ejecting of droplets described in block 516 and block 524 continues until control circuitry determines in block 520 that the complete pattern has been printed.

After printing of the pattern, the thin film layer is etched in block 528. Etching removes portions of the thin film not protected by the mask. The etching may be accomplished using a variety of acids and solvents common in thin-film semiconductor processing. After the etching of the thin-film layer, the masking layer  
5 may be removed as shown in block 532 using organic solvents such as tetrahydrofuran (THF).

The procedure described in Figure 5 allows for rapid direct marking. However, in some applications, the substrate to be patterned may be damaged by the phase-change masking layer. Alternately, the phase-change masking layer may not  
10 properly adhere to or coat the substrate to be patterned. In such instances, a sacrificial mask layer can be fabricated between the substrate to be etched and the phase-change material to avoid damaging the substrate or thin film surface to be patterned. The sacrificial mask layer is then patterned and serves as a mask for the substrate or thin film beneath it. Flow chart 600 of Figure 6 describes one embodiment of a sacrificial  
15 mask process.

In block 602 a thin-film to be etched is deposited and acts as a substrate to be patterned and etched. In block 604 of Figure 6, a thin-film sacrificial layer is deposited over the substrate to be patterned. An example of a typical sacrificial layer material is aluminum. In one embodiment, the thin-film layer is between 100 and 300  
20 nanometers thick. A phase-change material is printed over the sacrificial layer in block 608. The printing process uses a droplet source to deposit droplets of phase-change material similar to the procedure described in block 504 to block 524 of Figure 5.

In block 612, the thin film sacrificial layer is etched using an acid such  
25 as a mixture of sulfuric and phosphoric acid. After the thin-film sacrificial layer has been patterned, a second solvent etches the substrate in block 616 to remove the phase-change printed mask. The sacrificial layer such as aluminum, defined by the

printed phase-change mask material, then serves as a mask during the substrate etching process. After the substrate has been etched, the sacrificial layer is removed in block 620 using a removal compound such as a mixture of sulfuric and phosphoric acid. In other applications, the phase-change mask and the sacrificial layer may be used in combination to mask the underlying substrate surface during the etch process. Removal of the sacrificial layer usually includes removal of the phase-change material protecting the sacrificial layer. The removal of the phase-change material may precede or be concurrent with the removal of the sacrificial layer.

A third application of the phase-change mask material uses the phase-change mask in a photolithographic process. In the described process, printed phase-change masking material replaces the conventional aligner-plate mask traditionally used in photolithographic systems. Using a printed phase-change material such as wax instead of an aligner-plate avoids the need for a stepper/aligner to expose the patterned feature. Furthermore, the approach provides flexibility when compared to the direct masking processes described in Figure 5 and Figure 6 by providing a negative resist capability that allows masking of areas to be removed rather than masking of areas that are not to be etched. Such a capability is particularly useful when most of the substrate is to remain, and only small areas are to be removed.

Figure 7 shows a flow chart using the phase change mask material in a photolithographic process. In block 704 of Figure 7, a coating of photosensitive material is deposited on a substrate to be patterned. In one embodiment of the invention, the photosensitive material is a spin-on polymer such as SU-8. A phase change material is printed over the polymer layer in block 708. The printing process uses a droplet source to deposit droplets of phase change material similar to the procedure described in block 504 to block 524 of Figure 5.

After printing, the surface of the polymer is exposed to ultraviolet light in block 712. The ultraviolet light defines the polymer causing the polymer to

transform and crosslink allowing the masked regions to be removed. After processing of the polymer, the mask pattern is removed in block 716. The material protected by the mask pattern is also removed. In one embodiment of the invention, a tetrahydrofuran (THF) solution removes the mask pattern while allowing the SU8 to remain.

It should be understood that the foregoing description is intended to be illustrative of the invention. Variations and modification of the descriptions provided herein will present themselves to those skilled in the art. For example, the description has identified examples of phase-change materials, as well as different methods of causing a droplet to be ejected from a fluid reservoir. Examples of devices fabricated, such as a thin-film transistor have been described. However, other methods, other phase-change materials may also be used. Other devices may also be fabricated using the methods described herein. Accordingly, the present description should not be read as limiting the scope of the invention except as described in the claims that follow.